Thermal Energy Changes and their Effects on Organic Solvents' Raman Spectra

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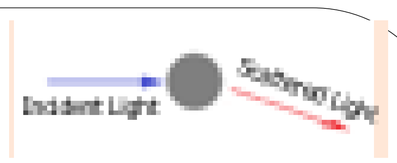
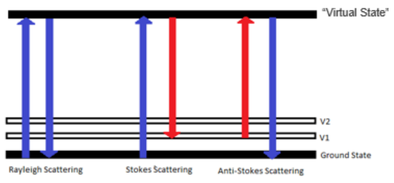
Background

- Raman Spectroscopy is the acquisition of a spectrum of inelastically scattered light from molecules



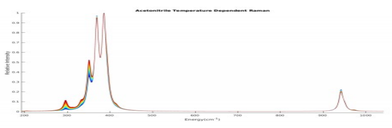


- The energy change that light incident upon a solvent molecule undergoes corresponds to the energy difference between two vibrational energy levels of the molecule: the starting vibrational energy and the vibrational energy of the molecule after the light scatters

- The population density of each "starting" vibrational energy level is related to the temperature of the solvent
- Computational models (Wang-Landau, WL) predicting the densities of vibrational energy states, DOS, have been created but have not been empirically supported

Motivation

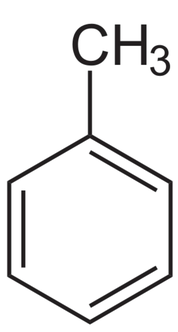
- Compare Raman Spectra at different temperatures to develop a qualitative understanding of how Raman shifts vary with temperature
- Quantitatively compare these shifts to what has been computationally predicted to occur by the WL model
- To aid in the understanding of cutting edge Raman laser spectroscopy that time resolve the changes in molecular vibrations as energy is transferred within or between molecules



Temperature Variant Computational Raman Spectrum for Acetonitrile

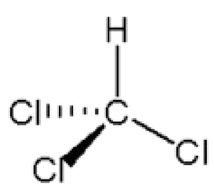
Methodology and Spectroscopic Advantages to Toluene, Chloroform, and Cyclohexane

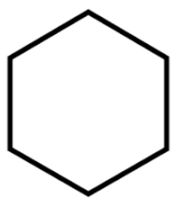
- Using a 633nm CW (Continuous Wave) Laser, Raman Spectra are collected for Toluene, Chloroform, and Cyclohexane



Toluene Structure

Chloroform Structure





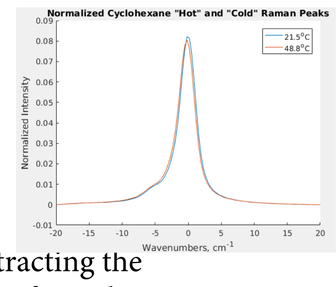
Cyclohexane Structure

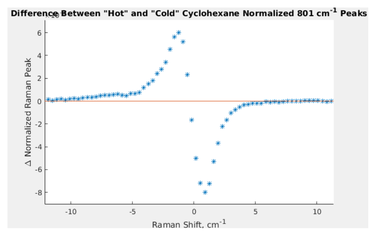
Toluene Advantages	Chloroform Advantages	Cyclohexane Advantages
Strong Raman Scattering	Easy to Model Computationally	Easily Isolable Raman Peak at 801 Wavenumbers

- Using a heating element, the temperature of the solvents were manually altered and recorded using a thermocouple
- The spectra were recorded at each temperature and compared to one another *and* the WL model

Analyzing "Hot" and "Cold" Raman Spectra

- Plotting "Hot" and "Cold" Raman spectra of cyclohexane at the 801 wavenumber peak shows a broadening and blueshifting of light with increased temperature



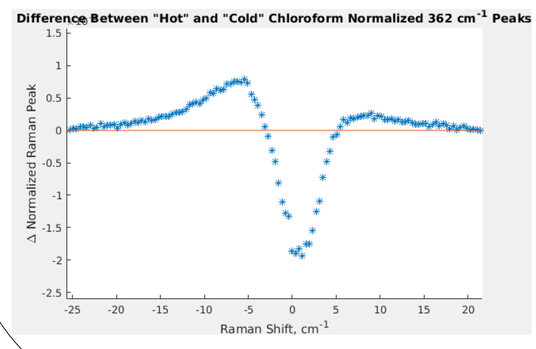


- Normalizing peaks and subtracting the "Cold" cyclohexane spectrum from the "Hot" Raman peak yields a differential shift towards higher energy (bluer) light

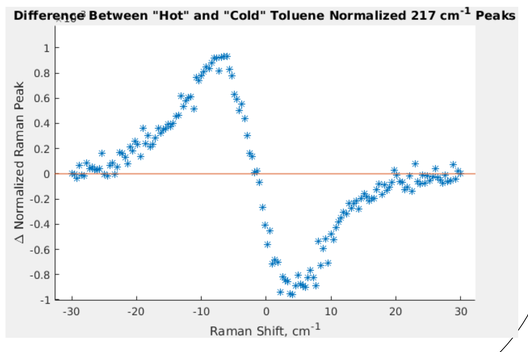
Chloroform and toluene echo the shift documented in cyclohexane

1. "Hotter" peaks broaden
2. "Hotter" peaks emit more energetic light than the colder solvents

Chloroform Shifting



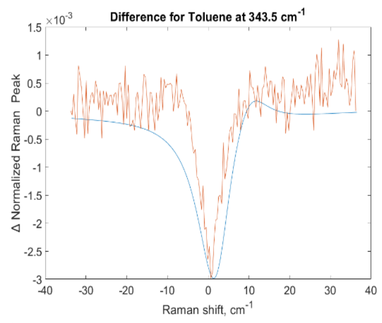
Toluene Shifting

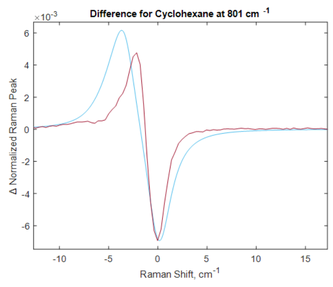


Computational Comparisons

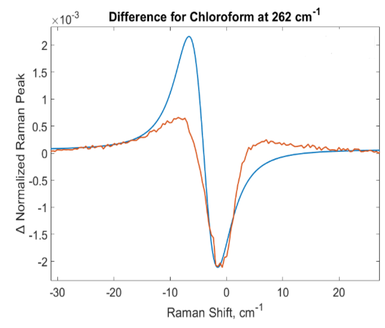
Qualitative Similarities between Computational and Experimental Spectra

1. Noticeable blue shift with higher temperature





2. The hotter solvents' raman peaks are broader than the colder raman solvents' peaks



The overall shift and broadening present in the experimental spectra is qualitatively represented in the computational spectra.

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